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(54) Title: CATALYST AND PROCESS FOR PRODUCING LOW-AROMATICS DISTILLATES

(57) Abstract

This invention provides a process for producing a distillate boiling-range hydrocarbon product which comprises hydrotreating a hydrodesulfurized aromatic, substantially dealkylated hydrocarbon feed produced by the catalytic cracking of a hydrocarbon fraction, the feed having an initial boiling point of at least 149 °C (300 °F), an aromatic content of at least 30 weight percent, a hydrogen content not more than 12 weight percent and a sulfur content of not more than 5000 ppmw, in the presence of a catalyst comprising an inorganic, non-layered, porous, crystalline phase material having pores with diameters of at least 1.3 nm (13 Å), and exhibiting, after calcination, an X-ray diffraction pattern with at least one peak with a relative intensity of 100 at a d-spacing greater than 1.8 nm (18 Å), the material containing at least one Group VIII metal and less than 5000 ppm Na, the process being carried out at a hydrogen partial pressure of not more than 1000 psig to evolve product containing less than 10 weight percent aromatics and less than 300 ppmw sulfur at a 390 °F+ feed conversion of less than 30 weight percent.

CATALYST AND PROCESS FOR PRODUCING LOW-AROMATICS DISTILLATES

The invention relates to a catalyst and process for
5   decreasing the aromatics content of a hydrodesulfurized
petroleum distillate, particularly a hydrodesulfurized,
catalytically cracked distillate boiling-range hydrocarbon
stock. The catalyst for this process comprises a Group
VIIIA metal, an M41S material, and preferably a binder.

10   Under present conditions, petroleum refineries are
finding it necessary to convert increasingly greater
proportions of crude to premium fuels including gasoline
and middle distillates such as diesel and jet fuel.
Catalytic cracking processes, exemplified by the fluid
15   catalytic cracking (FCC) process and Thermofor catalytic
cracking (TCC) process together, account for a substantial
fraction of heavy liquids conversion in modern refineries.
Both are thermally severe processes which result in a
rejection of carbon to coke and to residual fractions;
20   during catalytic cracking high molecular weight liquids
disproportionate into relatively hydrogen-rich light
liquids and aromatic, hydrogen-deficient heavier
distillates and residues.

Hydrocracking may be used to upgrade the higher-
25   boiling more refractory products derived from catalytic
cracking prior to the treatment in the present
hydrotreating process. Useful hydrocracking catalysts
include the catalysts taught in U.S. Patent 5,227,353, the
most prominent among which is a metallosilicate identified
30   as MCM-41 which is usually synthesized with Brønsted acid
sites by incorporating a tetrahedrally coordinated
trivalent element such as Al, Ga, B, or Fe within the
silicate framework.

Catalytic cracking therefore produces significant
35   quantities of highly aromatic, light and middle distillates
which not only have high sulfur and nitrogen levels, but
which may contain as much as 80 wt.% or more of aromatics.
Generally, the level of heteroatom contaminants increases

with the boiling point of the fraction. For example, the
light cycle oil produced as a typical FCC main column
bottoms stream contains about 80% aromatics, 4.6% sulfur
compounds, 1500 ppm nitrogen compounds, and about 9.1%
5   hydrogen (in proportions and percentages by weight, as in
the remainder of this specification unless otherwise
defined).

Present market requirements make highly aromatic
product streams such as these particularly difficult to
10   dispose of as commercially valuable products. Formerly,
the light and heavy cycle oils could be upgraded and sold
as light or heavy fuel oil, such as No. 2 fuel oil or No. 6
fuel oil. Upgrading the light cycle oil was conventionally
carried out by a relatively low severity, low pressure
15   catalytic hydrodesulfurization (CHD) unit in which the
cycle stock would be admixed with virgin middle distillates
from the same crude blend fed to the catalytic cracker.

At many petroleum refineries, the light cycle oil
(LCO) from the FCC unit is a significant component of the
20   feed to the catalytic hydrodesulfurization (CHD) unit which
produces No. 2 fuel oil or diesel fuel. The remaining
component is generally virgin kerosene taken directly from
the crude distillation unit. The highly aromatic nature of
LCO, particularly when the FCC unit is operated in the
25   maximum gasoline mode, increases operational difficulties
for the CHD and can result in a product having marginal
properties for No. 2 fuel oil or diesel oil, as measured by
cetane numbers and sulfur content. Further, increasingly
stringent environmental regulations limiting the aromatics
30   content of diesel fuel have prompted refiners to focus
research efforts on economical methods for producing the
required low-aromatics fuels.

An alternative market for middle distillate streams is
automotive diesel fuel. However, diesel fuel has to meet a
35   minimum cetane number specification of about 45 in order to
operate properly in typical automotive diesel engines.

Because cetane number correlates closely and inversely with aromatic content, the highly aromatic cycle oils from the cracker typically with aromatic contents of 80% or even higher have cetane numbers as low as 4 or 5. In order to raise the cetane number of these cycle stocks to a satisfactory level by the conventional CHD technology described above, substantial and uneconomic quantities of hydrogen and high pressure processing would be required.

Thus from an economic and operational standpoint, it would be desirable to rely upon the CHD unit for desulfurization, and to provide a more effective and less costly method for reducing aromatics content while providing a product which closely matches the boiling ranges of the feedstock.

The hydrotreating catalyst of the invention comprises a Group VIIIA metal on a mesoporous crystalline material having a a substantially uniform hexagonal honeycomb microstructure with uniform pores having a cell diameter greater than 1.3 nm (13 Å) and typically in the range of 2 to 10 nm (20 to 100 Å). The mesoporous crystalline material typically has a framework SiO_2/Al_2O_3 ratio of greater than 20.0, and contains less than 0.5 wt% Na. The catalyst composition preferably includes a binder or a matrix material. The term "Group VIIIA metal" as used herein refers to Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt as shown in the Periodic Table of the Elements published as Catalog No. S-18806 by Sargent-Welch Scientific Company, 7300 North Linder Avenue, Skokie, Illinois, 60077.

This invention provides a process for producing a distillate boiling-range hydrocarbon product which comprises hydrotreating an aromatic, substantially dealkylated hydrocarbon feed produced by the catalytic cracking of a hydrocarbon fraction, which feed has been catalytically hydrodesulfurized, the feed having an initial boiling point of at least 149°C (about 300°F), an aromatic content of at least 30 weight percent, a hydrogen content

not more than 10.0 weight percent and a sulfur content of not more than 5000 ppmw, in the presence of a catalyst comprising an inorganic, non-layered, porous, crystalline phase material having pores with diameters of at least 1.3

5   nm (about 13 Å) and exhibiting, after calcination, an X-ray diffraction pattern with at least one peak with a relative intensity of 100 at a d-spacing greater than 1.8 nm (about 18 Å) to evolve product containing less than 10 weight percent aromatics and less than 300 ppmw sulfur. The

10 operating pressure usually falls within the range of 7000 to 8400 kPa (from about 1000 to about 1200 psig).

The hydrotreating catalyst of this invention has an unusually low activity for boiling range conversion, thus producing a product having essentially the same boiling

15 range as the feed. In one embodiment, the process of this invention is characterized by a 199°C conversion (390°F+ conversion) of less than 30 wt%, preferably less than 20 wt%, and more preferably less than 10 wt%. As used herein, the term "199°C+ conversion" ("390°F+ conversion") is

20 defined as follows:

$$199°C+ \; conversion = \left\{ \frac{(199°C+ \; in \; feed) - (199°C+ \; in \; product)}{199°C+ \; in \; feed} \right\}$$

$$\left(390°F+ \; conversion = \left\{ \frac{(390°F+ \; in \; feed) - (390°F+ \; in \; product)}{390°F+ \; in \; feed} \right\} \right)$$

In another embodiment, the process of this invention characterized by a 149°C+ conversion (300°F+ conversion) of

25 less than 30 wt%, preferably less than 20 wt%, and more preferably less than 10 wt%. As used herein, the term "149°C+ conversion" ("300°F+ conversion") is defined as follows:

$$149°C+ \ conversion = \left\{ \frac{(149°C+ \ in \ feed) \ - \ (149°C+ \ in \ product)}{(149°C+ \ in \ feed)} \right\}$$

$$\left(300°F+ \ conversion = \left\{ \frac{(300°F+ \ in \ feed) \ - \ (300°F+ \ in \ product)}{300°F+ \ in \ feed} \right\} \right)$$

The feed is preferably hydrotreated (hydro-
desulfurized) upstream from the process of the present
invention to reduce sulfur content in the feed to less than
5000 ppmw, preferably less than 1000 ppmw, more preferably
5   less than 300 ppmw. In a particularly preferred
embodiment, the feed is hydrodesulfurized to less than 50
ppmw sulfur.

The hydrotreating is operated under low to moderate
pressure, typically 2860 - 8380 kPa (400 - 1200 psig)
10   hydrogen pressure. At the relatively low severity
conditions employed temperatures will generally be in the
range 315°- 455°C (600° - 850 F), more preferably from 290°
to 455°C (about 550 to about 700°F) to maximize aromatics
conversion.

15   Figure 1A is a plot of 199°C+ (390°F+) feed conversion
as a function of reaction temperture for a Pd/RE-USY/Al₂O₃
catalyst (datapoints represented by open circles) and a
Pd/MCM-41/Al₂O₃ (datapoints represented by solid circles).

Figure 1B is a plot of product aromatics content as a
20   function of reaction temperature for a Pd/RE-USY/Al₂O₃
catalyst (datapoints represented by open circles) and
Pd/MCM-41/Al₂O₃ (datapoints represented by solid circles).

Figure 2A is a plot of hydrogen consumption in
standard cubic feet per barrel of hydrocarbon feed as a
25   function of reaction temperature for a Pd/RE-USY/Al₂O₃
catalyst (datapoints represented by open circles) and
Pd/MCM-41/Al₂O₃ (datapoints represented by solid circles).

Figure 2B is a plot of hydrogen consumption in
standard cubic feet per barrel of hydrocarbon feed as a

function of total aromatics in the product for a Pd/RE-USY/Al$_2$O$_3$ catalyst (datapoints represented by open circles) and Pd/MCM-41/Al$_2$O$_3$ (datapoints represented by solid circles).
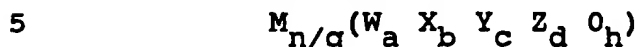
5   Mesoporous Crystalline Component

The mesoporous crystalline component of the catalyst is described in detail below. When it is used in the present catalysts, the mesoporus crystalline material is at least partly in the decationized or hydrogen form in order to provide the desired functionality for the reactions

10   which are to take place.

The mesoporous catalytic material is an inorganic, porous, non-layered crystalline phase material which can be characterized (in its calcined form) by an X-ray

15   diffraction pattern with at least one peak at a d-spacing greater than 1.8 nm (about 18 Å) with a relative intensity of 100 and a benzene sorption capacity of greater than 15 grams of benzene per 100 grams of the the material at 345 kPa (50 torr) and 25°C. The X-ray pattern should be

20   determined with the metal-free material since the presence of the metal component, particularly at high metal loadings, may obscure the X-ray pattern.

The preferred form of the crystalline material has a hexagonal arrangement of uniformly-sized pores with a

25   maximum perpendicular cross-section pore dimension of at least 1.3 nm (13 Angstroms (Å)), and typically within the range of from 1.3 nm to 20 nm (13 Å to 200 Å). A preferred form of this hexagonal crystalline composition, identified as MCM-41, exhibits a hexagonal electron diffraction

30   pattern that can be indexed with a d$_{100}$ value greater than 1.8 nm (18 Å), and a benzene adsorption capacity of greater than about 15 grams benzene/100 grams crystal at 345 kPa (50 torr) and 25°C. This material is described in detail in U.S. Patents 5,098,684 and 5,102,643 to Kresge et al.,
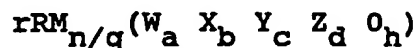
35   and below.

The inorganic, non-layered mesoporous crystalline material used as a component of the catalyst has the following composition:

$$M_{n/q}(W_a \: X_b \: Y_c \: Z_d \: O_h)$$

wherein W is a divalent element, such as a divalent first row transition metal, e.g. manganese, cobalt and iron, and/or magnesium, preferably cobalt; X is a trivalent element, such as aluminum, boron, iron and/or gallium, preferably aluminum; Y is a tetravalent element such as silicon and/or germanium, preferably silicon; Z is a pentavalent element, such as phosphorus; M is one or more ions, such as, for example, ammonium, Group IA, IIA and VIIB ions, usually hydrogen, sodium and/or fluoride ions; n is the charge of the composition excluding M expressed as oxides; q is the weighted molar average valence of M; n/q is the number of moles or mole fraction of M; a, b, c, and d are mole fractions of W, X, Y and Z, respectively; h is a number of from 1 to 2.5; and (a+b+c+d) = 1.

A preferred embodiment of the above crystalline material is when (a+b+c) is greater than d, and h = 2. A further embodiment is when a and d = 0, and h = 2. The preferred materials for use in making the present hydrotreating catalysts are the aluminosilicates.

In the as-synthesized form, the catalytic material has a composition, on an anhydrous basis, expressed empirically as follows:

$$rRM_{n/q}(W_a \: X_b \: Y_c \: Z_d \: O_h)$$

where R is the total organic material not included in M as an ion, and r is the coefficient for R, i.e. the number of moles or mole fraction of R.

The M and R components are associated with the material as a result of their presence during crystallization, and are easily removed or, in the case of

M, replaced by post-crystallization methods described below.

To the extent desired, the original M, e.g. sodium or chloride, ions of the as-synthesized material of this

5 invention can be replaced in accordance with conventional ion-exchange techniques. Preferred replacing ions include metal ions, hydrogen ions, hydrogen precursor, e.g. ammonium, ions and mixtures of these ions. Particularly preferred ions are those which provide the desired metal

10 functionality in the final hydrotreating catalyst. These include hydrogen, rare earth metals and metals of Groups VIIA (e.g. Mn), VIIIA (e.g. Ni),IB (e.g. Cu), IVB (e.g. Sn) of the Periodic Table of the Elements and mixtures of these ions.

15 The crystalline (i.e. having sufficient order to provide a diffraction pattern such as, for example, by X-ray, electron or neutron diffraction, following calcination with at least one peak) mesoporous material may be characterized by its structure, which includes extremely

20 large pore windows as well as by its high sorption capacity. The term "mesoporous" is used here to indicate crystals having uniform pores within the range of from 1.3 nm to 20 nm (13 Å to 200 Å). The mesoporous materials have uniform pores within the range of from 1.3 nm to 20 nm (13

25 Å to 200 Å), more usually from 1.5 nm to 10 nm (15 Å to 100 Å). Since these pores are significantly larger than those of other crystalline materials, it is appropriate to refer to them as ultra-large pore size materials. For the purposes of this application, a working definition of

30 "porous" is a material that adsorbs at least 1 gram of a small molecule, such as Ar, N_2, n-hexane or cyclohexane, per 100 grams of the solid.

The catalytic material can be distinguished from other porous inorganic solids by the regularity of its large open

35 pores, whose pore size more nearly resembles that of amorphous or paracrystalline materials, but whose regular

arrangement and uniformity of size (pore size distribution
within a single phase of, for example, $\pm$ 25%, usually $\pm$ 15%
or less of the average pore size of that phase) resemble
more those of crystalline framework materials such as

5 zeolites. The preferred materials have a hexagonal
arrangement of large open channels that can be synthesized
with open internal diameters from 1.3 nm to 20 nm (13 Å to
200 Å). The term "hexagonal" is intended to encompass not
only materials that exhibit mathematically perfect

10 hexagonal symmetry within the limits of experimental
measurement, but also those with significant observable
deviations from that ideal state. A working definition as
applied to the microstructure of the present invention
would be that most channels in the material would be

15 surrounded by six nearest neighbor channels at roughly the
same distance. Defects and imperfections will cause
significant numbers of channels to violate this criterion
to varying degrees, depending on the quality of the
material's preparation. Samples which exhibit as much as $\pm$

20 25% random deviation from the average repeat distance
between adjacent channels still clearly give recognizable
images of the present ultra-large pore materials.
Comparable variations are also observed in the d_{100} values
from the electron diffraction patterns.

25   The most regular preparations of the material of the
present invention give an X-ray diffraction pattern with a
few distinct maxima in the extreme low angle region. The
positions of these peaks approximately fit the positions of
the hk0 reflections from a hexagonal lattice. The X-ray

30 diffraction pattern, however, is not always a sufficient
indicator of the presence of these materials, as the degree
of regularity in the microstructure and the extent of
repetition of the structure within individual particles
affect the number of peaks that will be observed. Indeed,

35 preparations with only one distinct peak in the low angle
region of the X-ray diffraction pattern have been found to

contain substantial amounts of the material in them. Other
techniques to illustrate the microstructure of this
material are transmission electron microscopy and electron
diffraction. Properly oriented specimens of the material
show a hexagonal arrangement of large channels and the
corresponding electron diffraction pattern gives an
approximately hexagonal arrangement of diffraction maxima.
The d_{100} spacing of the electron diffraction patterns is
the distance between adjacent spots on the hk0 projection
of the hexagonal lattice and is related to the repeat
distance a_0 between channels observed in the electron
micrographs through the formula $d_{100} = a_0 \sqrt{3}/2$. This d_{100}
spacing observed in the electron diffraction patterns
corresponds to the d-spacing of a low angle peak in the X-
ray diffraction pattern of the material. The most highly
ordered preparations of the material obtained so far have
20-40 distinct spots observable in the electron diffraction
patterns. These patterns can be indexed with the hexagonal
hk0 subset of unique reflections of 100, 110, 200, 210,
etc., and their symmetry-related reflections.

In its calcined form, the crystalline material may be
further characterized by an X-ray diffraction pattern with
at least one peak at a position greater than 1.8 nm (18
Angstrom) Units d-spacing (4.909° 2θ for Cu K-alpha
radiation) which corresponds to the d_{100} value of the
electron diffraction pattern of the material, and an
equilibrium benzene adsorption capacity of greater than 15
grams benzene/100 grams crystal at 345 kPa (50 torr) and
25°C (basis: crystal material having been treated in an
attempt to insure no pore blockage by incidental
contaminants, if necessary).

The equilibrium benzene adsorption capacity
characteristic of this material is measured on the basis of
no pore blockage by incidental contaminants. For instance,
the sorption test will be conducted on the crystalline
material phase having any pore blockage contaminants and

water removed by ordinary methods. Water may be removed by
dehydration techniques, e.g. thermal treatment. Pore
blocking inorganic amorphous materials, e.g. silica, and
organics may be removed by contact with acid or base or
5   other chemical agents such that the detrital material will
be removed without detrimental effect on the crystal.

More particularly, the calcined crystalline non-
layered material may be characterized by an X-ray
diffraction pattern with at least two peaks at positions
10   greater than 1 nm (10 Angstrom Units) d-spacing (8.842 °θ
for Cu K-alpha radiation), at least one of which is at a
position greater than 1.8 nm (18 Angstrom Units) d-spacing,
and no peaks at positions less than 1 nm (10 Å) d-spacing
with relative intensity greater than 20% of the strongest
15   peak. Still more particularly, the X-ray diffraction
pattern of the calcined material of this invention will
have no peaks at positions less than 1 nm (10 Å) d-spacing
with relative intensity greater than 10% of the strongest
peak. In any event, at least one peak in the X-ray
20   diffraction pattern will have a d-spacing that corresponds
to the d_{100} value of the electron diffraction pattern of
the material.

The calcined inorganic, non-layered crystalline
material may also be characterized as having a pore size of
25   1.3 nm (13 Å) or greater as measured by physisorption
measurements, described below. Pore size is considered a
maximum perpendicular cross-section pore dimension of the
crystal.

X-ray diffraction data were collected on a Scintag PAD
30   X automated diffraction system employing theta-theta
geometry, Cu K-alpha radiation, and an energy dispersive X-
ray detector. Use of the energy dispersive X-ray detector
eliminated the need for incident or diffracted beam
monochromators. Both the incident and diffracted X-ray
35   beams were collimated by double slit incident and
diffracted collimation systems. The slit sizes used,

starting from the X-ray tube source, were 0.5, 1.0, 0.3 and 0.2 mm, respectively. Different slit systems may produce differing intensities for the peaks. The materials of the present invention that have the largest pore sizes may

5 require more highly collimated incident X-ray beams in order to resolve the low angle peak from the transmitted incident X-ray beam.

The diffraction data were recorded by step-scanning at 0.04 degrees of 2θ, where θ is the Bragg angle, and a

10 counting time of 10 seconds for each step. The interplanar spacings, d's, were calculated in Å (A), and the relative intensities of the lines, I/I_o, where I_o is one-hundredth of the intensity of the strongest line, above background, were derived with the use of a profile fitting routine.

15 The intensities were uncorrected for Lorentz and polarization effects. The relative intensities are given in terms of the symbols vs = very strong (75-100), s = strong (50-74), m = medium (25-49) and w = weak (0-24). The diffraction data listed as single lines may consist of

20 multiple overlapping lines which under certain conditions, such as very high experimental resolution or crystallographic changes, may appear as resolved or partially resolved lines. Typically, crystallographic changes can include minor changes in unit cell parameters

25 and/or a change in crystal symmetry, without a substantial change in structure. These minor effects, including changes in relative intensities, can also occur as a result of differences in cation content, framework composition, nature and degree of pore filling, thermal and/or

30 hydrothermal history, and peak width/shape variations due to particle size/shape effects, structural disorder or other factors known to those skilled in the art of X-ray diffraction.

The equilibrium benzene adsorption capacity is

35 determined by contacting the material of the invention, after dehydration or calcination at, for example, about

540°C for at least about one hour and other treatment, if
necessary, in an attempt to remove any pore blocking
contaminants, at 25°C and 50 torr benzene until equilibrium
is reached. The weight of benzene sorbed is then
5   determined as described below.

The ammonium form of the catalytic material may be
readily converted to the hydrogen form by thermal treatment
(calcination). This thermal treatment is generally
performed by heating one of these forms at a temperature of
10   at least 400°C for at least 1 minute and generally not
longer than 20 hours, preferably from 1 to 10 hours. While
subatmospheric pressure can be employed for the thermal
treatment, atmospheric pressure is desired for reasons of
convenience, such as in air, nitrogen, ammonia, etc. The
15   thermal treatment can be performed at a temperature up to
about 750°C. The thermally treated product is particularly
useful in the catalysis of certain hydrocarbon conversion
reactions.

Synthesis methods useful for preparing the mesoporous
20   crystalline component of the invention is taught in U.S.
Patents 5,227,353 to Apelian et al., and 5,102,643 to
Kresge et al.

Catalyst Metal Component

The catalyst of the invention comprises a mesoporous
25   crystalline material as described below. The catalyst
further comprises a Group VIIIA noble metal, and platinum
and palladium are particularly preferred noble metal
components.

The content of the metal component will vary according
30   to its catalytic activity. Thus, the highly active noble
metals may be used in smaller amounts than the less active
base metals. For example, 1 wt. percent or less platinum
will be effective and in a preferred base metal
combination, 7 wt. percent nickel and 2.1 to 40 wt. percent
35   tungsten, expressed as metal. The present support

materials are, however, notable in that they are capable of
including a greater proportion of metal than previous
support materials because of their extraordinarily large
surface area. The metal component may exceed 25 percent
5   and still maintain a high surface area above 200 $m^2 g^{-1}$.
The metal component can be exchanged onto the support
material, impregnated into it or physically admixed with
it. If the metal is to be impregnated into or exchanged
onto the mesoporous support, it may be done, for example,
10   by treating the zeolite with a platinum metal-containing
ion. Suitable platinum compounds include chloroplatinic
acid, platinous chloride and various compounds containing
the platinum ammine complex. The metal compounds may be
either compounds in which the metal is present in the
15   cation of the compound and compounds in which it is present
in the anion of the compound. Both types of compounds can
be used. Platinum compounds in which the metal is in the
form of a cation of cationic complex, e.g., $Pt(NH_3)_4Cl_2$ are
particularly useful, as are anionic complexes such as the
20   vanadate and metatungstate ions. Cationic forms of other
metals are also very useful since they may be exchanged
onto the crystalline material or impregnated into it.

Mesoporous catalysts similar to those disclosed here
are described also in U.S. Patent 5,288,395 which discloses
25   mesoporous lube hydrocracking catalysts and U.S. Patent
5,173,286 which discloses mesoporous catalysts used for wax
hydrocracking/hydroisomerization.

Feedstocks

The feedstocks used in the present process are
30   hydrocarbon fractions which are highly aromatic, which may
also be hydrogen deficient, and which can contain up to 0.5
wt% sulfur. These feedstocks generally comprise fractions
which have been substantially dealkylated, as by a
catalytic cracking operation, for example, in an FCC or TCC
35   unit. Catalytic cracking characteristicly removes alkyl

groups (generally bulky, relatively large alkyl groups,
typically but not exclusively C_5-C_9 alkyls), which are
attached to aromatic moieties in the feed. These detached
alkyl groups form the bulk of the gasoline product from the
5   cracker. The aromatic moieties such as benzene,
naphthalene, benzothiophenes, dibenzothiophenes and
polynuclear aromatics (PNAs) such as anthracene and
phenanthrene form the high boiling products from the
cracker. The mechanisms of acid-catalyzed cracking and
10   similar reactions remove side chains of greater than 5
carbons while leaving behind short chain alkyl groups,
primarily methyl, but also ethyl groups on the aromatic
moieties. Thus, the "substantially dealkylated" cracking
products include those aromatics with small alkyl groups,
15   such as methyl, and ethyl, and the like still remaining as
side chains, but with relatively few large alkyl groups,
i.e., the C_5-C_9 groups remaining. More than one of these
short chain alkyl groups may be present, for example, one,
two or more methyl groups.
20   Feedstocks of this type may have an aromatic content
in excess of 50 wt. percent; for example, 70 wt. percent or
80 wt. percent or more, aromatics. Highly aromatic feeds
of this type typically have hydrogen contents below 14 wt.
percent, usually below 12.5 wt. percent or even lower, e.g.
25   below 10 wt. percent or 9 wt. percent. The API gravity is
also a measure of the aromaticity of the feed, usually
being below 30 and in most cases below 25 or even lower,
e.g. below 20. In most cases the API gravity will be in
the range 5 to 25 with corresponding hydrogen contents from
30   8.5-12.5 wt. percent. Because the feeds useful in the
process of this invention are desulfurized, the feeds
typically contain less than 5000 ppmw sulfur, preferably
less than 1000 ppmw sulfur, more preferably less than 300
ppmw sulfur. In a particularly preferred embodiment, the
35   feed contains no more than 50 ppmw sulfur. The nitrogen

content of the feed typically ranges from 50 to 1000 ppmw, more usually from 50 to 650 ppmw.

Suitable feeds for the present process are substantially dealkylated cracking product fractions.

5   Suitable feeds of this type include cycle oils from catalytic cracking units. Full range cycle oils may be used, for example, full range light cycle oils with a boiling range of 195° - 400°C (385°-750°F), e.g., 205° - 370°C (400°-700°F) or, alternatively, cycle oil fractions

10   may be employed such as heavy cycle oil or light cycle oil fractions. When operating with an extended boiling range feeds such as a full range light cycle oil (FRLCO), conversion should be limited so as to avoid excessive catalyst aging; a maximum conversion to a product

15   containing 5 wt% aromatics is preferred. However, if a light cut cycle oil is used, higher conversions may be tolerated. For this reason, lower boiling range fractions of that type are preferred. Thus, cycle oils with end points below 345°C (650°F), preferably below 315°C (600°F)

20   are preferred. Initial boiling point will usually be 150°C (300°F) or higher, e.g. 165°C (330°F) or 195°C (385°F).

Feeds having higher endpoints tend to age the catalyst of the invention more rapidly. For this reason, less severe operating conditions (principally LHSV and

25   temperature) are preferred for higher endpoint feeds. In a preferred embodiment, the maximum feedstock endpoint is 399°C (750°F), more preferably 370°C (700°F). Light cycle oils generally contain from 60 to 80% aromatics and, as a result of the catalytic cracking process, are substantially

30   dealkylated, as described above. Other examples of suitable feedstocks include the dealkylated liquid products from delayed or fluid bed coking processes. If a cycle oil fraction is to be used, it may be obtained by fractionation of a full range light cycle oil or by adjustment of the cut

35   points on the catalytic cracker fractionation column.

   While the aromatics content of the product stream
varies with process severity, the product typically
contains less than 20 weight percent aromatics, preferably
less than 15 weight percent aromatics, and more preferably
5   below 10 weight percent aromatics.

   This process decreases aromatics content without
substantially changing the boiling range of the feedstock.
In contrast, U.S. Patent 5,219,814 to Kirker et al. teaches
a process using an ultrastable zeolite Y catalyst which
10   cracks the feedstock to lighter products.

   The invention will now be illustrated by the following
Examples.

EXAMPLES

Example 1

15   A USY zeolite with a framework SiO_2/Al_2O_3 ratio of 200
(as measured by Al-NMR) and no detectable silanol content
(as measured by Si-NMR) was exchanged with a rare earth
chloride solution at pH = 5.   65 parts by weight of this
RE-exchanged USY was mixed with 35 parts by weight Al_2O_3 on
20   a dry basis.   Enough water was added to form an extrudable
paste.   This mixture was formed into 1.59 mm (1/16")
extrudates.   The extrudates were dried at 121°C (250°F) and
air calcined at 538°C (1000°F) for 3 hours.   The calcined
extrudates were humidified and then exchanged with a
25   solution containing $Pd(NH_3)_4^{++}$.   The Pd-containing
extrudates were then calcined at 288°C (550°F).   This
material is referred to as Catalyst A and has properties
summarized in Table 1.

Example 2

30   An MCM-41S catalyst was prepared in accordance with
the procedure of U.S. Patent 5,102,643 to Kresge et al.

Example 3

   65 parts by weight of the MCM-41S material prepared in
Example 2 (which contained a high concentration of silanol

groups) was ammonium exchanged, dried, and then mixed with 35 parts by weight Al_2O_3 on a dry basis. Enough water was added to form an extrudable paste. This mixture was formed into 1.59 mm (1/16") extrudates. The extrudates were dried

5   at 121°C (250°F), heated to 482°C (900°F) in N_2, held in N_2 for 6 hours, and air calcined at 538°C (1000°F) for 9 hours. The calcined extrudates were humidified and then exchanged with a solution containing $Pd(NH_3)_4^{++}$. The Pd-containing extrudates were then calcined at 288°C (550°F).

10 This material is referred to as Catalyst B and has properties summarized in Table 1.

Example 4

The catalysts described above in Examples 1 and 2 were used to treat a low-sulfur (<10 ppmw) distillate fuel

15 containing 45 wt% aromatics (Feed-I, Table 2). Example 3 demonstrates catalyst performance for hydrogenation of low-sulfur fuels derived from a conventional high-pressure (7105 kPa (>1000 psig)) hydrotreating process. Each catalyst was crushed and sized to 14/24 mesh, and evaluated

20 at 1 LHSV and 7105 kPa (1000 psig) H_2 pressure. Each catalyst was reduced in 2550 kPa (350 psig) H_2 at 177°C (350°F) for three hours prior to introducing the feed. The results for the three catalysts are summarized in Table 3 and Figures 1A through 2B. While both catalysts reduce

25 aromatics content to below 5 wt%, Catalyst B gives a higher yield of low-aromatics distillate while consuming less hydrogen. Further, Catalyst B exhibits a lower activation energy for conversion to products having atmospheric boiling points at or below 199°C (390°F).

Example 5

30 Catalyst A and Catalyst B were evaluated using a feedstock produced from a conventional catalytic hydrodesulfurizer (4410 kPa (625 psig)), Co-Mo or Ni-Mo hydrodesulfurization catalyst). The feedstock (Feed-II,

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Table 2) produced from the CHD unit contained 500 ppmw
sulfur, 41.3 wt% aromatics, and 200 ppmw nitrogen.
Results are shown in Table 4. Catalyst A was effective in
reducing aromatics content with only a minor loss in yield.
5   Catalyst B, on the other hand, appears to be most
applicable for feeds containing less than 0.05 wt% sulfur.

Table 1
Catalyst Properties

	Catalyst A	Catalyst B
Crystalline Catalytic Material	USY	MCM-41
Framework SiO_2/Al_2O_3	200	40
Crystalline Catalytic Material, wt.%	65	65
Binder	Al_2O_3	Al_2O_3
Binder wt.%	35	35
RE_2O_3, wt.%	0.09	-
Palladium, wt.%	0.63	0.83
Sodium, ppmw	320	78
C_γ-C_6 Sorption, wt.%	16.9	-
Pore Volume, g/ml	0.67	0.97
Particle Density, g/ml	0.95	0.73
Surface area, m^2/g	451	682
Chemisorption		
H/Pd ratio	0.74	1.06
O/Pd ratio	0.54	0.52

Table 2
Feedstocks Properties

	Feed-I	Feed-II
Gravity, API	31.8	32.1
Sulfur, ppmw	<10	500
Nitrogen, ppmw	2	200
Aromatics (ASTM-M1539)	45	41.3
Distillation (ASTM-D2887)		
Weight Percent	Temperature, °C (°F)	
5	172 (341)	184 (363)
30	253 (488)	237 (458)
50	283 (541)	267 (513)
70	311 (592)	298 (569)
95	369 (697)	355 (672)

Table 3
Summary of Example 3

- Yield and Conversion based on 199°C (390°F) cut point
- Catalyst A: Pd/(200/1) USY/Al$_2$O$_3$
- Catalyst B: Pd/MCM-41/Al$_2$O$_3$

	Feed-I	Product from reaction with Catalyst A	Product from reaction with Catalyst B
LHSV	-	1.0	1.0
Pressure, kPa (psig)	-	7000 (1000)	790 (100)
LHSV, hr^{-1}	-	1.0	1.0
Temperature, °C (°F)	-	316 (600)	316 (600)
Conversion, wt.%	-	44.4	21.7
Yield, wt.%	97.7	54.3	76.6
H$_2$ Consumption, SCF/B (Standard Cubic Feet per Barrel of Feed)	-	1491	1432
Sulfur, ppmw	<12	<10	<10
Aromatics, wt.%	45	2.7	<1.0

Table 4
Summary of Example 4

• Yield and Conversion based on 199°C (390°F) cut point

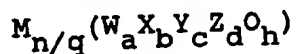|	Feed	Product from reaction with Catalyst A	Product from reaction with Catalyst B
LHSV	-	1.0	1.0
Pressure, kPa (psig)	-	7000 (1000)	7000 (1000)
LHSV, hr⁻¹	-	1.0	1.0
Temperature, °C (°F)	-	343 (650)	343 (650)
Conversion, wt.%	-	15.5	1.1
Yield, wt.%	91.0	76.9	90.0
H₂ Consumption, v/v of feed (SCF/B (Standard Cubic Feet per Barrel of Feed))	-	33000 (1853)	10400 (584)
Sulfur, ppmw	500	<10	260
Desulfurization, %	-	96	48
Aromatics, wt.%	41.3	8.3	40.6

Changes and modifications in the specifically described embodiments can be carried out without departing from the scope of the invention which is intended to be limited only by the scope of the appended claims.

CLAIMS:

1.   A process for producing a distillate boiling-range
      hydrocarbon product which comprises hydrotreating a
      hydrodesulfurized aromatic, substantially dealkylated
5   hydrocarbon feed produced by the catalytic cracking of
      a hydrocarbon fraction, the feed having an initial
      boiling point of at least 149°C, an aromatic content
      of at least 30 weight percent, a hydrogen content not
      more than 12 weight percent and a sulfur content of
10   not more than 5000 ppmw, in the presence of a catalyst
      comprising an inorganic, non-layered, porous,
      crystalline phase material having pores with diameters
      of at least 1.3 nm and exhibiting, after calcination,
      an X-ray diffraction pattern with at least one peak
15   with a relative intensity of 100 at a d-spacing
      greater than 1.8 nm, the material containing at least
      one Group VIII metal and less than 5000 ppm Na to
      evolve product containing less than 10 weight percent
      aromatics and less than 300 ppmw sulfur at a 199°C+
20   feed conversion of less than 30 weight percent.

2.   A process acccording to claim 1 in which the
      crystalline phase material has, after calcination, a
      hexagonal arrangement of uniformly-sized pores with
      diameters of at least 1.3 nm and exhibits a hexagonal
5   electron diffraction pattern that can be indexed with
      a d_{100} value greater than 1.8 nm.

3.   The process of claim 1 in which the crystalline phase
      has an X-ray diffraction pattern following calcination
      with at least one peak whose d-spacing corresponds to
10   the d_{100} value from the electron diffraction pattern.

4. The process of claim 1 in which the crystalline phase exhibits a benzene adsorption capacity of greater than 15 grams benzene per 100 grams at 345 kPa and 25°C.

5. The process of claim 1 in which the crystalline phase has a composition expressed as follows:

$$M_{n/q}(W_a X_b Y_c Z_d O_h)$$

wherein M is one or more ions; n is the charge of the composition excluding M expressed as oxides; q is the weighted molar average valence of M; n/q is the number of moles or mole fraction of M; W is one or more divalent elements; X is one or more trivalent elements; Y is one or more tetravalent elements; Z is one or more pentavalent elements; a, b, c, and d are mole fractions of W, X, Y, and Z, respectively; h is a number of from 1 to 2.5; and (a+b+c+d) = 1.

6. The process of claim 4 wherein W comprises a divalent first row transition metal or magnesium; X comprises aluminum, boron, gallium or iron; Y comprises silicon or germanium; and Z comprises phosphorus.

7. The process of claim 4 wherein a and d are 0 and h = 2.

8. The process of claim 7 wherein X comprises aluminum, boron, gallium or iron and Y comprises silicon or germanium.
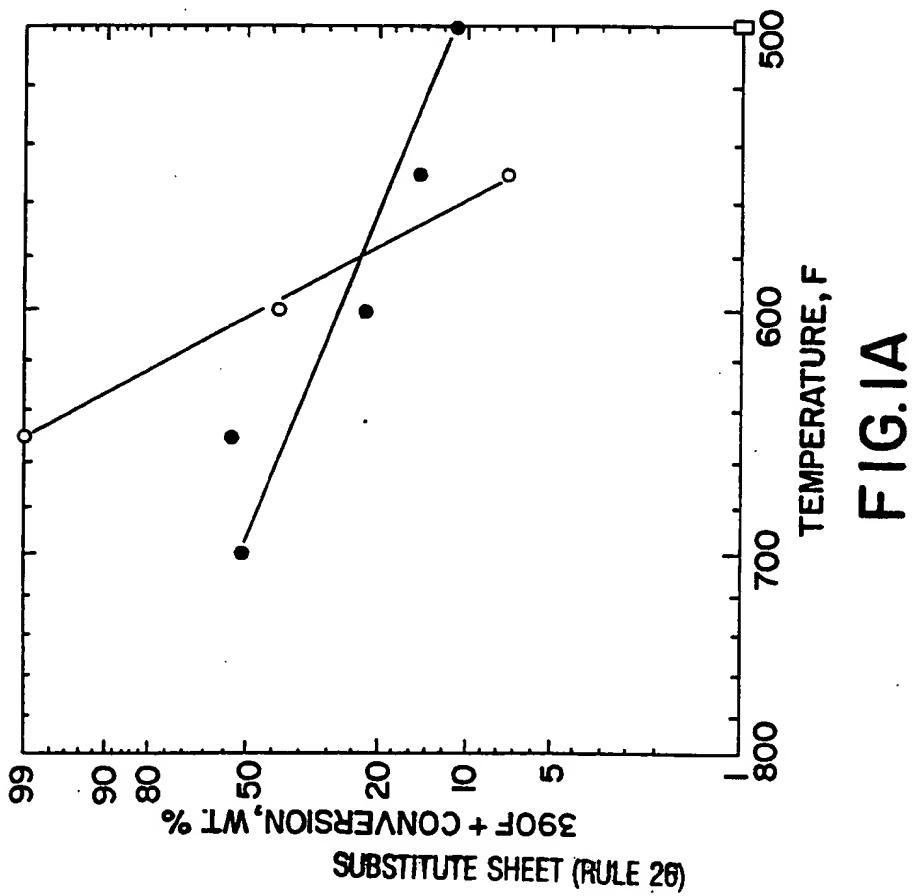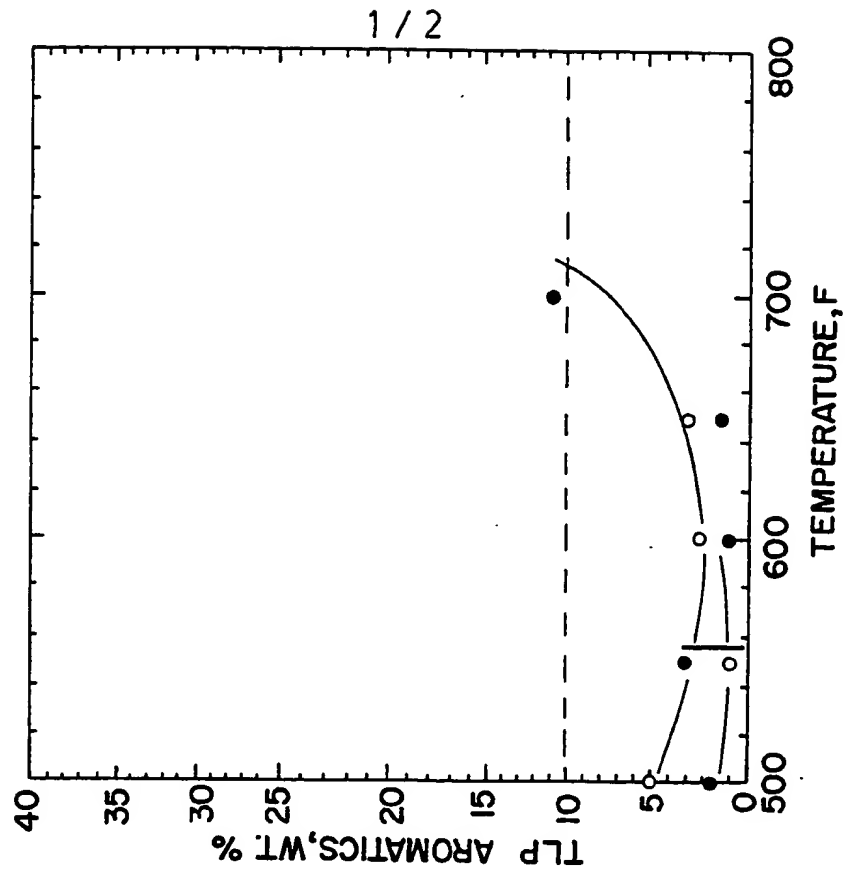
9. The process of claim 8 wherein X comprises aluminum and Y comprises silicon.

10. The process of claim 1 in which the catalyst comprises at least one metal of Groups VIA, VIIA or VIIIA of the Periodic Table.

11. The process of claim 1 in which the catalyst comprises at least one metal of Group VIA and at least one metal of Group VIIIA of the Periodic Table.

12. The process of claim 1 in which the feed is contacted with the catalyst at a pressure of from 2860 to 8377 kPa, a temperature from 260° to 454°C.

13. The process of claim 12 in which the feed is contacted with the catalyst at a temperature from 288° to 399°C.

14. The process of claim 5, in which the distillate comprises the fraction boiling above 196°C.

15. The process of claim 5, in which the feed comprises a hydrodesulfurized catalytic cracking cycle oil.

16. The process of claim 5, in which the feed has a hydrogen content of 8.5 to 12.5 weight percent.

17. The process of claim 5, in which the feed has an API gravity not more than 25.

18. The process of claim 1 in which the 199°C+ feed conversion is less than 20 weight percent.

19. The process of claim 18 in which the 300°F+ feed conversion is less than 20 weight percent.

20. The process of claim 1 wherein the endpoint of the hydrodesulfurized feedstock is less than 399°C.

21. The process of claim 1 wherein the catalyst comprises at least 0.1 wt% of the Group VIIIA metal.

22. The proces of claim 1 wherein the Group VIIIA metal is selected from the group consisting of platinum and palladium.

23. The process of claim 1 wherein the product contains less than 15 weight percent aromatics.
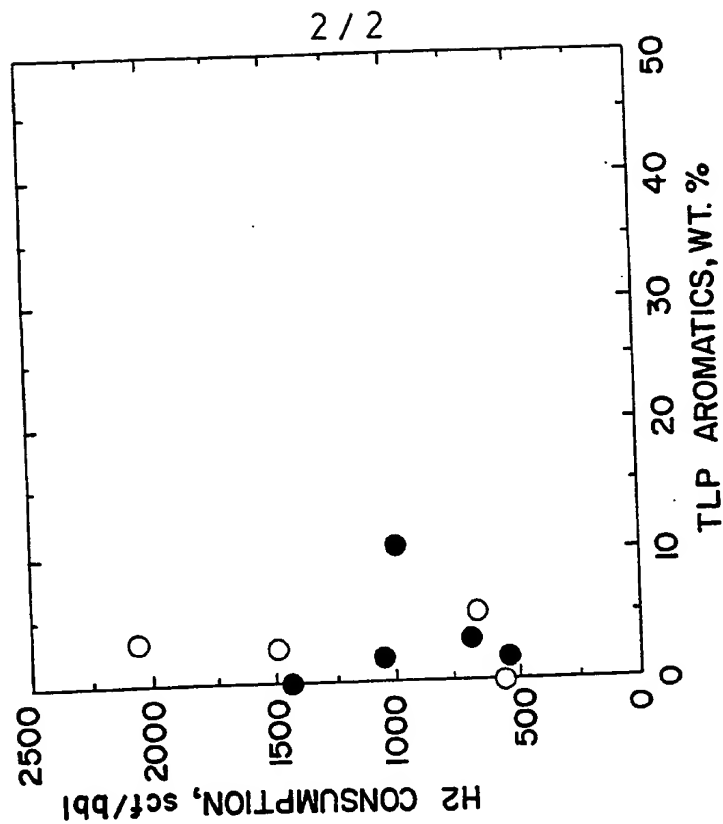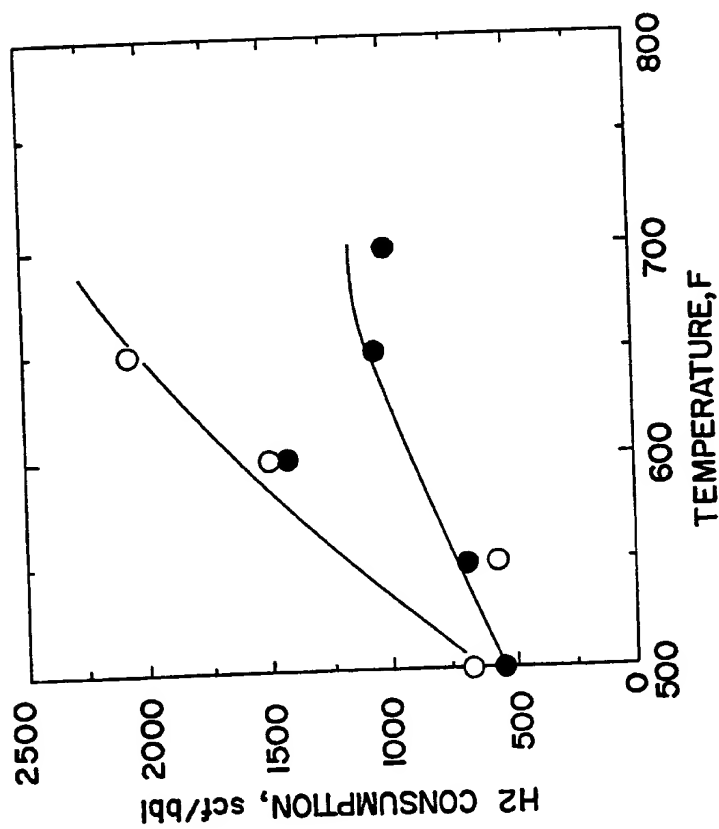
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FIG.IB

FIG.IA

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FIG.2B

FIG.2A

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C10G 45/54, 45/52
US CL :208/143, 144; 585/266, 269, 273, 275

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/143, 144; 585/266, 269, 273, 275

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5,102,643 (KRESGE ET AL) 07 APRIL 1992	1-23
A	US, A, 5,219,814 (KIRKER ET AL) 15 JUNE 1993	1-23
A	US, A, 5,227,353 (APELIAN ET AL) 13 JULY 1993	1-23
P, A	US, A, 5,264,641 (BORGHARD ET AL) 23 NOVEMBER 1993	1-23

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 NOVEMBER 1994	03 JAN 1995

Name and mailing address of the ISA/US	Authorized officer
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